FINAL REPORT

New Ionic Liquids from Natural Products for Environmentally Benign Aircraft Deicing and Anti-Icing

SERDP Project WP-1679

DECEMBER 2010

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Naval Air Warfare Center Weapons Division

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SERDP SEED PROJECT (WP-1679) FINAL REPORT: New Ionic Liquids from Natural Products for Environmentally Benign Aircraft Deicing and Anti-Icing

Naval Air Warfare Center
China Lake, California

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List of Acronyms

ASTM	American Society for Testing and Materials
BOD_5	biochemical oxygen demand (5 day)
C_p	heat capacity
EC_{50}	effective concentration to immobilize 50% microorganism
GRAS	'generally regarded as safe', Food & Drug Administration
ILs	ionic liquids
$J \cdot mol^{-1} \cdot K^{-1}$	unit of measure for heat capacity (Joules per moleKelvin)
LC_{50}	effective concentration at which 50% of the organism population died
pH	hydronium ion concentration, acidity
RTILs	room-temperature ionic liquids

SAE	Society of Automotive Engineers
ThOD	theoretical oxygen demand

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Abstract

Under exploratory development (SEED) funding from the Strategic Environmental Research and Development Program (SERDP), ionic liquids composed of naturally-occurring anions were synthesized and evaluated as environmentally benign deicing fluids. Exothermic dissolution and low freezing point depression of water were promising. However, calculations of theoretical oxygen demand as well as toxicity appear to preclude these ionic liquids from 'drop-in' replacement deicing formulations.

Objective

The proposed work will be focused on mitigation of technical risks associated with the development of new deicing and anti-icing material formulations based on ionic liquids (ILs) derived from natural products. The first steps will involve identifying compositions of ILs made from naturally-occurring organic salts that are both liquid at room temperature as well as highly water soluble. Testing of the ionic liquid compositions will be directed at demonstrating the possibilities for compliance with key aspects of SAE ANSI 1424 and 1428 along with corrosion prevention, compatibility with key aircraft parts, viscosity, residue, biochemical oxygen demand, and aquatic toxicity.

1. Background

Ice that forms on the wings of military aircraft affects flight performance and therefore must be completely removed before aircraft takeoff. The typical deicing method involves spraying an aircraft's wings with a hot 80/20 mixture of propylene glycol/water just before takeoff. Although propylene glycol is 'generally regarded as safe' (GRAS) by the US Food & Drug Administration, there is a negative impact on the environment from the large biochemical oxygen demand (BOD) created during the metabolism of the propylene glycol by aquatic microorganisms. In addition, the propylene glycol based mixtures contain toxic additives. The Environmental Protection Agency will soon enact stricter regulations regarding the runoff from deicing operation at airports. An environmentally benign deicer would thus bring tremendous benefits to military and civilian airfields.

Ionic liquids (ILs) are, in all known instances, bimolecular complexes of an anion and a cation. Over the last ten years, many new ILs have been prepared and studied as replacements for common organic solvents used in the chemical industry. It appears, however, that the use of ILs has not been applied substantially to the problem of aircraft wing deicing. A close concept has been experimented with recently by the Finnish Air Force. They tested the commercial product Betafrost®, Danisco A/S Copenhagen, which is a 50% aqueous solution of the natural product trimethylglycine for deicing of aircraft and tarmac, Figure 1.

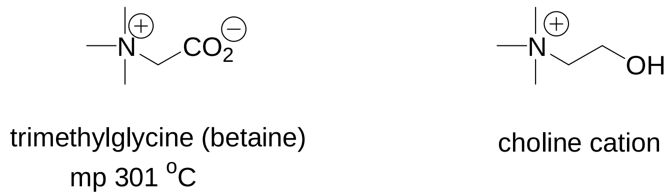


Figure 1. Chemical structures of betaine and choline.

The deicing performance of the trimethylglycine solution was comparable to inorganic systems such as potassium acetate and had low BOD and low corrosion capacity of metals. However, trimethylglycine is a high melting solid that leaves behind a residue upon evaporation from water. The physical properties of ILs are wide ranging, though; some have vitrification temperatures below -60°C. The physical properties of ILs may be tuned easily by altering the chemical composition of the constituent anions and cations.

Included in the large array of available anions and cations are many non-toxic natural products. Choline is used by all organisms in the biochemical synthesis and maintenance of cell membranes (Figure 1). Also, choline plays a role in signal transduction by neuronal cells after esterification to acetylcholine. As its chloride salt, choline is manufactured on the metric ton scale primarily as an animal feed additive. Used as a cation, the preparation of ILs from choline and two GRAS food ingredients (artificial sweeteners), saccharine and acesulfamate was recently published. The resulting ILs, choline saccharinate and sulfamate, exhibited low ecotoxicity (EC_{50} ~1300 mg/L) in a bioassay with the invertebrate *Daphnia magna*. In comparison, the synthetic imidazolium-based ILs were quite toxic (EC_{50} ~14 mg/L) in the same bioassay. Both ILs are water soluble, however they are crystalline solids at room temperature. It has recently been shown that the combination of choline and propionic or tiglic acids (Figure 2) resulted in a truly room temperature ILs composed of naturally occurring ions, which are completely water soluble.

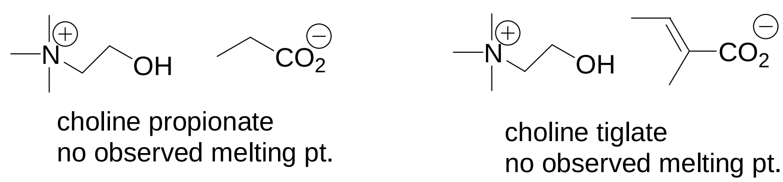


Figure 2. Chemical structures of liquid choline salts.

It appears then that choline may be combined with soft anions from carboxylic acids or α-amino acids, such as citric acid, glutamic acid and proline to form ILs with low melting points, Figure 3. In this way, the resulting ILs will be composed completely of GRAS molecules with low environmental toxicity.

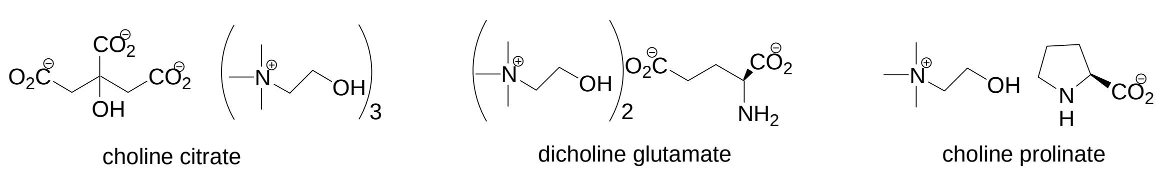


Figure 3. Potentially new choline salts.

2. Materials and Methods

Betaine, ethanolamine, tris-(2-hydroxyethyl)-methylammonium methyl sulfate, diethanolamine, choline hydroxide 45 wt% in methanol, choline acetate, 1-butyl-3-methylimidazolium chloride, formic acid, lactic acid, levulinic acid, acetic anhydride, propionic acid, glycolic acid, glycine, sulfamic acid, pyruvic acid, dimethylsulfate, butyric acid, pivalic acid, tetramethylammonium hydroxide, trifluoroacetic acid, saccharine were purchased from Sigma-Aldrich (Milwaukee).

2.1 Synthesis of the ionic liquids:

The ILs could be synthesized either by ion-exchange chromatography or by neutralization of commercial choline hydroxide, Figures 4 and 5. The latter method was used for the most part for simplicity. To a solution of the choline hydroxide in methanol was added an equivalent of the acid and after stirring 1 h the methanol was rotary evaporated leaving the crude IL containing 1 equivalent of water. The crude product was then placed under high vacuum (0.1 torr) for 24 h at 60 °C to remove the water of reaction as far as possible.

Typical method for the synthesis of the ionic liquids are shown below

1. Ion exchange chromatography

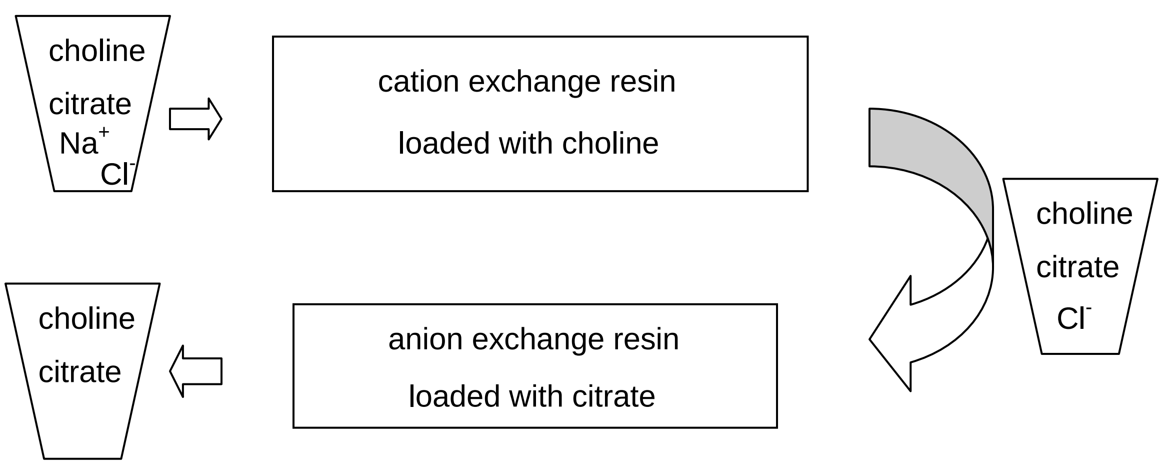
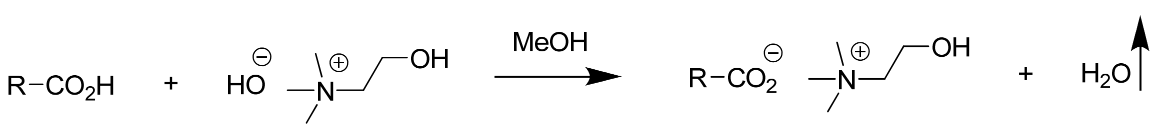


Figure 4. Anion exchange method of IL synthesis.

2. Neutralization



$$R\text{-}CO_2H + R_2NH \rightarrow RCO_2^- \, R_2NH_2^+ + H_2O\uparrow$$

Figure 5. Neutralization method of IL synthesis.

Sixteen choline based ILs were synthesized and their structures are shown in Figure 6. And five ethanolamine based ILs were also synthesized as a comparison, Figure 7. The ionic liquids synthesized were characterized by nuclear magnetic resonance and elemental analysis (see Supporting Data). Because of the tenacity with which the ILs retain the water from reaction, the elemental analyses data (C,H,N) were off a few percent from theory. Figure 8 shows some photos of the resulting ILs.

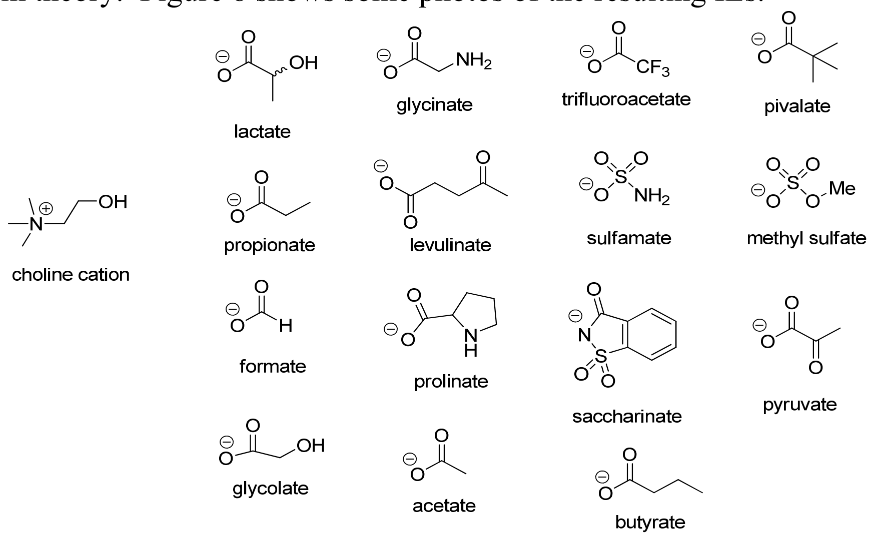


Figure 6. Structures of choline based ionic liquids synthesized.

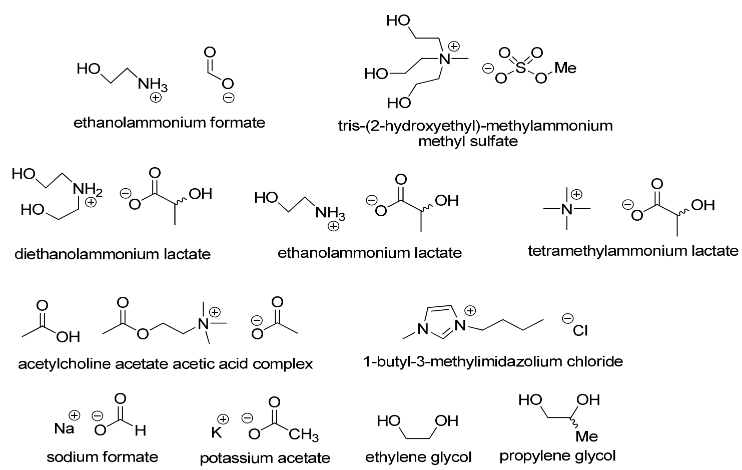


Figure 7. Structures of other types of ionic liquids.

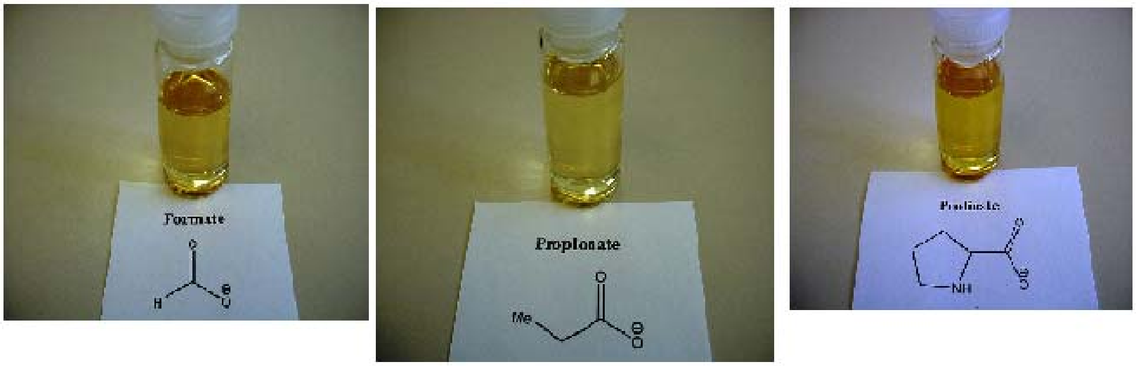


Figure 8. Photo of three choline ionic liquids.

2.2 Toxicity Analysis

Toxicity tests were conducted at the Wisconsin State Laboratory of Hygiene (Madison, WI, USA). Microtox® assays (Azur Environmental, Carlsbad, CA) were conducted to determine EC_{50} values for the luminescent marine bacterium *Vibrio fischeri* (formerly *Photobacterium phosphoreum*), Figure 9. The change in light emission was recorded over a series of dilution of test compound. Acute toxicity tests against the freshwater fish *Pimephales promelas* (fathead minnow, 96 hour) and the freshwater crustacean *Ceriodaphnia dubia* (waterflea, 48 hour) over a series of dilutions gave LC_{50} values. The latter were conducted following standard U.S. EPA methods. The LC_{50} ("lethal concentration 50") predicts the concentration of the studied compound that would cause 50% of the test population to die (in the case of *C. dubia* and *P. promelas*) and the EC_{50} ("effect concentration 50") predicts the concentration of the studied compound that would cause a reduction in light emission to 50% of control (in the case of the Microtox® assay). Detailed procedures for these experiments have been published previously.

Ceriodaphnia dubia   Pimephales promelas or fathead minnow   Vibrio fischeri

Figure 9. Photos of organisms used for toxicity studies.

3. Results and Discussion

Phase 1 testing and evaluation results are presented in this section.

3.1 Physical State of Ionic Liquids

Ionic liquids are relatively new chemical species and their physical properties can not be readily predicted. For deicing purposes, the ILs should be liquid at room temperature, the so called room-temperature ionic liquids (RTILs) and they should also be water soluble. This way they can be readily used in current deicing technologies such as sprayers and pumps. Several liquid ILs were identified and, typically, only these compounds were selected for further study, Table 1. In addition, all the ILs made here were completely water soluble which is not always the case as in the imidazolium-type ILs.

Table 1. Physical state of ILs at room-temperature.

Ionic Liquid	Physical State at Room Temperature
Choline formate	Liquid
Choline acetate	Solid
Choline propionate	Liquid
Choline butyrate	Solid
Choline pivalate	Solid
Choline trifluoroacetate	Solid
Choline lactate	Liquid
Choline prolinate	Liquid
Choline glycinate	Liquid
Choline levulinate	Liquid
Choline sulfamate	Solid
Choline glycolate	Solid
Choline pyruvate	Liquid
Choline saccharinate	Solid
Choline methyl sulfate	Solid
Ethanolammonium formate	Liquid
Tris-(2-hydroxyethyl)-methylammonium methyl sulfate	Liquid
Diethanolammonium lactate	Liquid
Ethanolammonium lactate	Liquid
Tetramethylammonium lactate	Solid
Acetylcholine acetate acetic acid complex	Liquid

3.2 Freezing Point Depression

The goal was set to meet or exceed the freezing point requirements set forth in SAE Aerospace Material Specification 1424 (AMS 1424). For Type I fluids, the lowest operational use temperature is established at -15 ºC. Those materials that can provide freezing point depression to -15 ºC may be a suitable replacement candidate. The ionic liquids were diluted with water to 50% to ensure that formulations developed can be appreciably diluted with water without freezing and meet hold-over time requirements. Freezing point depression results in Table 2 show that 6 out of 9 choline based ionic liquids exceed the requirements of AMS 1424. It should be repeated that all of these choline salts are readily soluble in water. And so it is interesting that even though choline acetate and choline pivalate are solids at room temperature, they both depress the freezing point of water sufficiently unlike the solid sulfamate and trifluoroacetate choline salts. This may be the result of the stronger anionic character of the counter ions sulfamate, methyl sulfate and trifluoroacetate with a concominant weak hydrogen bonding to water that doesn't disrupt the crystallization of water sufficiently (see Figure 10 below).

Table 2. Freezing Point Depression of Water by Ionic Liquids,
50% in water incubated at -30 C for 24 h.

Ionic Liquid	Physical State
Choline propionate	liquid
Choline acetate	liquid
Choline pivalate	liquid
Choline prolinate	liquid
Choline lactate	liquid
Choline formate	liquid
Choline sulfamate	solid
Choline trifluoroacetate	solid
Tris(2-hydroxyethyl)-methylammonium methyl sulfate	solid

3.3 Heat of Solution

The ILs synthesized all had an exothermic heat of solution when dissoved in water. This can be explained by the high hydrogen bonding capacity of the choline cation as well as each of the cations. For example, dissolving 30 g of the IL choline propionate in 30 g of 23 °C water caused an increase in temperature to 36 °C. Since the number of bonds created during dissolution are greater and stronger than the bonding of the initial ionic liquid, the result is an exothermic heat of solution, Figure 10.

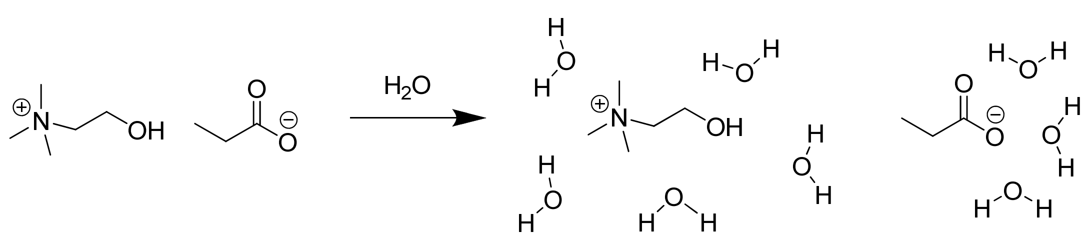


Figure 10. Exothermic dissolution of choline propionate.

3.4 Materials Compatibility

The advantage of these ionic liquids is that they are all typified by a pH ≈ 7 (the pH of choline propionate is 7.4) since they are essentially the salt of a base and acid which makes them less aggressive to metals. The set of ionic liquids were tested against 6061 aluminum test coupons by total immersion as outlined in ASTM F483. All the coupons showed little, if any observable discoloration after incubation for almost 8 weeks. At this time, corrosion testing of 1025 carbon steel has not been performed

3.5 Biodegradation

To determine the readily biodegradability of a composition, the composition may be tested using one or more of the tests described under OECD 301. In one embodiment, readily biodegradability is determined by a respirometry method, such as OECD 301B, OECD 301C, OECD 301D or OECD 301F, having pass levels for ready biodegradability based on 60% of theoretical oxygen demand ("ThOD"). After reading through the literature, it became readily apparent that these procedures were too difficult to carry out in-house. However, in the 1980's, BASF AG, a European manufacturer, had shown that choline chloride is readily biodegradable according to OECD-criteria (93 % biodegradation within 14 days) in a MITI I-Test (MITI, 1992). This result can be confirmed by Tunkel *et al.* (2000) who stated that a biodegradation of 60 % in a MITI-I test corresponds to a ready biodegradation. In addition, in a BOD_5 test performed according to DIN 38409 part 43 a $BOD_5/ThOD_5$ ratio of 75 % obtained, which also confirms a ready biodegradation of choline chloride (BASF AG, 1984).

But the calculations shown below appeared to make further research into the BOD_5 of these ILs a moot point. For example, in equations 1 and 2 the theoretical oxygen demand for the ionic liquid choline lactate is calculated to be 1.98 g of oxygen for each gram choline lactate, assuming that the nitrogen atom is converted to ammonia. In equation 3, every gram propylene glycol requires only 1.68 g oxygen for complete breakdown. Therefore, in regards of BOD, it is clear that these ILs will not be competetive with glycol based deicing formulations.

$$C_5H_{14}NO{\cdot}C_3H_4O_3 + 10\ O_2 \rightarrow 8\ CO_2 + NH_3 + 8\ H_2O \quad \textbf{\textit{equation 1}}$$
$$NH_3 + 2\ O_2 \rightarrow HNO_3 + H_2O \quad \textbf{\textit{equation 2}}$$

1 mol choline lactate = 193 g/mol
1 mol O_2 = 32 g/mol
Thus (10 + 2) * 32/193 = 1.98 g O_2 / g choline lactate

$$C_3H_8O_2 + 4\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O \quad \textbf{\textit{equation 3}}$$

1 mol propylene glycol = 76 g/mol
1 mol O_2 = 32 g/mol
Thus 4 * 32/76 = 1.68 g O_2 / g propylene glycol

3.6 Toxicity Studies

The runoff from airport deicing activities readily enters surface water reaching nearby streams and waterways, eventually entering oceans. Three aquatic organisms were selected for gauging the impact the release of these materials would have on the aquatic environment. Only ILs that were liquid at room temperature, so called room-temperature ionic liquids or RTILs, were selected for study since these would make the best candidates for deicing. The toxicity data for the ILs and additional compounds is shown in Table 3. Of the organisms used in the studies, it appears that *C. dubia* shows the greatest sensitivity to all substances tested. For the choline based ILs (**6**-**12**): the LC_{50} for *C. dubia* was in the range of 296-451 mg/L; and the LC_{50} for fathead minnow was 2,210-14,865 mg/L; and the EC_{50} in the Microtox® assay varied between 45-12,891 mg/L. The 'protic' ILs (**3**-**5**) had similar toxicity as the choline based RTILs. Compounds **3**-**5** were all 2-3 times less toxic to *C. dubia* than the choline RTILs.

Some other compounds were included in the toxicity studies to give a wider picture. For example, betaine, which is a commercial deicing product sold as a 50% aqueous solution (Betafrost®) and used by the Finnish Air Force, is indeed rather non-toxic even to *C. dubia*. This is no surprise since betaine is a naturally occurring substance used by organisms to modulate osmotic pressure. The IL **2** or BASIONIC™ FS 01 is a commercial product from BASF marketed as an 'ecologically friendly' RTIL. This is true to a certain extent, but again the compound has a level of toxicity to *C. dubia*. Also, the 'synthetic' imidazolium-based IL **13** was tested as a comparison to the 'green' ILs prepared in this study. As can be seen, **13** is very toxic to the microorganisms but less so to fish. And it is much more toxic than any of the choline RTILs used in this study. This imidazolium happens to be water soluble and it is known that lengthening the alkyl chain increases toxicity as well as decreasing water solubility.

Some other data taken from the literature was included in the toxicity table to get a better picture of deicing materials in general. Pavement deicing compounds such as the alkali metal salts of formic and acetic acids **14** and **15** have only modest toxicity to the organisms tested. And the pure glycols **16** and **17** are very non-toxic to all the species tested. However, the actual glycol deicing product is much more toxic, which results from the addition of an 'additive package' for corrosion protection and stabilization that includes many toxic organic compounds.

Table 3. Toxicity values for substances.

#	Test Substance	Microtox® EC_{50} (mg/L)	*C. dubia* LC_{50} (mg/L)	Fathead minnow LC_{50} (mg/L)
1	Betaine	185,119	6,699	34,020
2	Tris(2-hydroxyethyl)-methylammonium methyl sulfate	202,083	714	25,000
3	Ethanolammonium formate	2,180	1,120	2,210
4	Diethanolammonium lactate	96,667	620	8,839
5	Ethanolammonium lactate	10,046	597	3,716
6	Choline levulinate	2,561	451	14,865
7	Acetylcholine acetate (HOAc)	314	336	324
8	Choline lactate	12,891	364	14,865
9	Choline propionate	2,474	340	8,839
10	Choline glycolate	2,094	296	12,500
11	Choline formate	659	364	3,716
12	Choline glycinate	45.3	317	2,210
13	1-butyl-3-methylimidazolium chloride	246	5.9	1,581
14	Potassium Acetate	6,440[a]	313[a]	421[a]
15	Sodium Formate	23,000[a]	1400[a]	2300[a]
16	Ethylene Glycol	133,000[b]	34,400[b]	72,900[b]
17	Propylene Glycol	83,500[b]	18,300[b]	55,800[b]
18	Commercial Type I Deicer Fluid (88% propylene glycol)	14,400[c]	7,850[c]	12,300[c]

[a] Corsi, S.R.; Geis, S.W.; Bowman, G.;Failey, G.G.; Rutter, T.D *Environ. Sci. Technol.* **2009**, *43*, 40-46. [b] Pillard, D.A. *Environ. Toxicol. Chem.* **1997**, *14*, 311-315. [c] Corsi, S.R.; Geis, S.W.; Loyo-Rosales, J.E.; Rice, C.P. *Environ. Sci. Technol.* **2006**, *40*, 7409-7415.

4. Conclusions and Implications for Future Research/Implementation

These ILs appear to have excellent freezing-point depression of water. Coupled to, presumably, high heat capacities, these ILs might be much more efficient at deicing than glycol-based products. The ILs described here are much less toxic and therefore 'greener' than the typical commercial imidazolium-type ILs. However, from a toxicity and oxygen demand stand-point, these choline-based ILs will not make a direct replacement of current deicing formulations used at airfields. However, they may be useful as a kind of surfactant that could be added to these deicing products to decrease the toxicity of the 'additive package' contained in these products.

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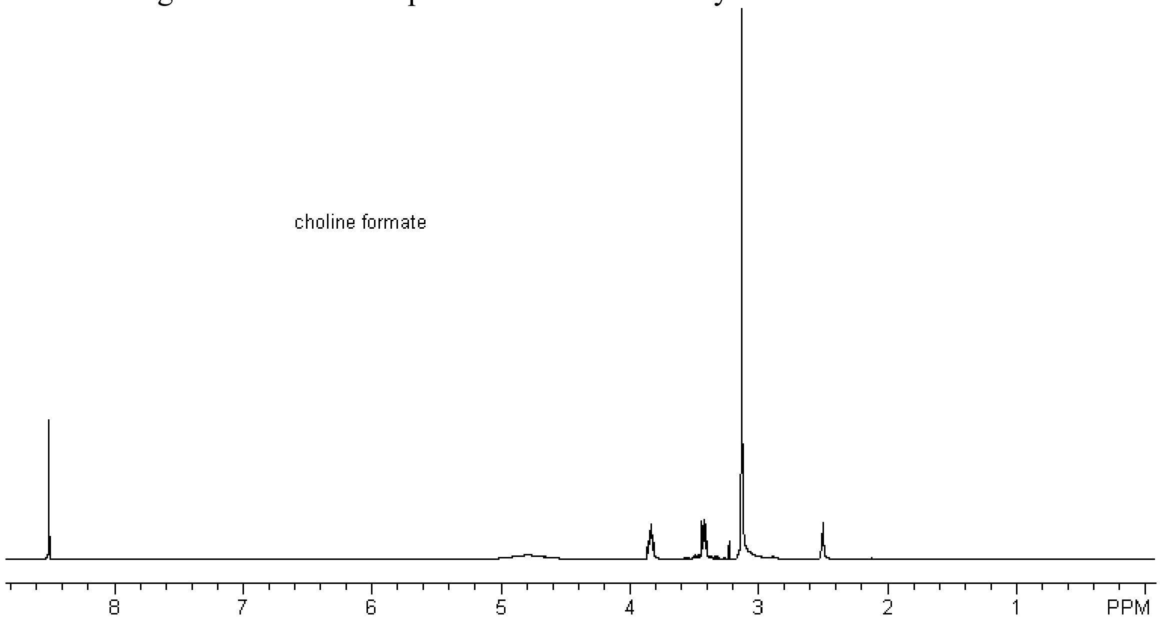
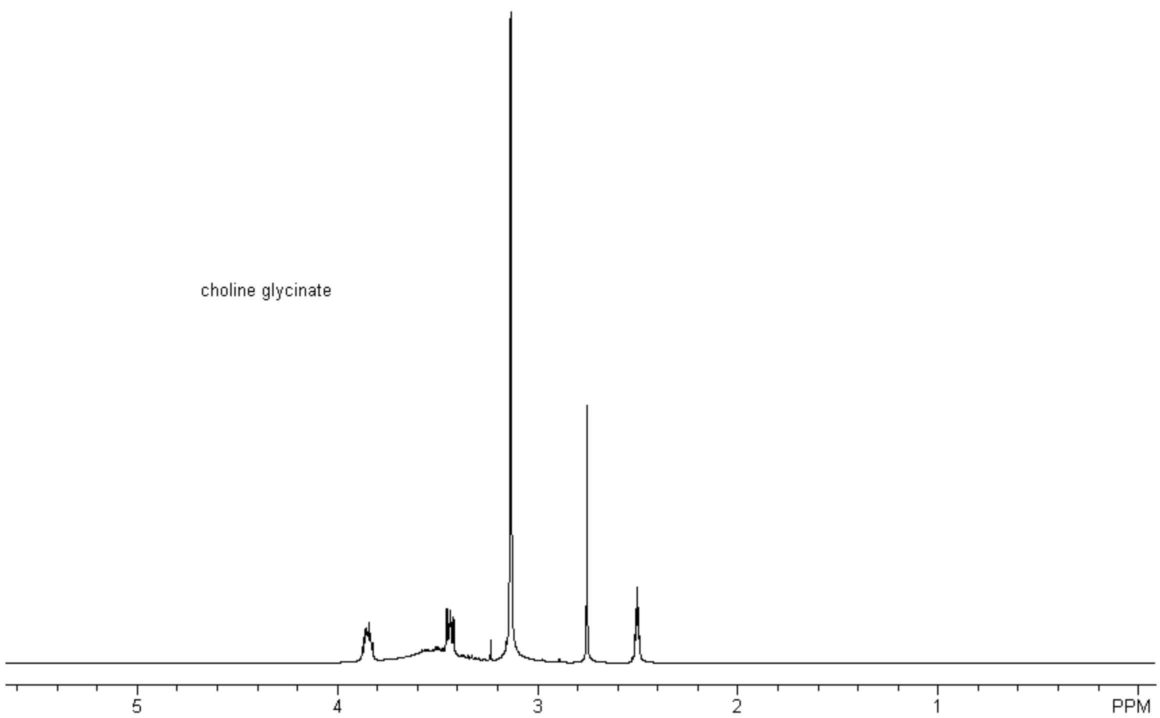
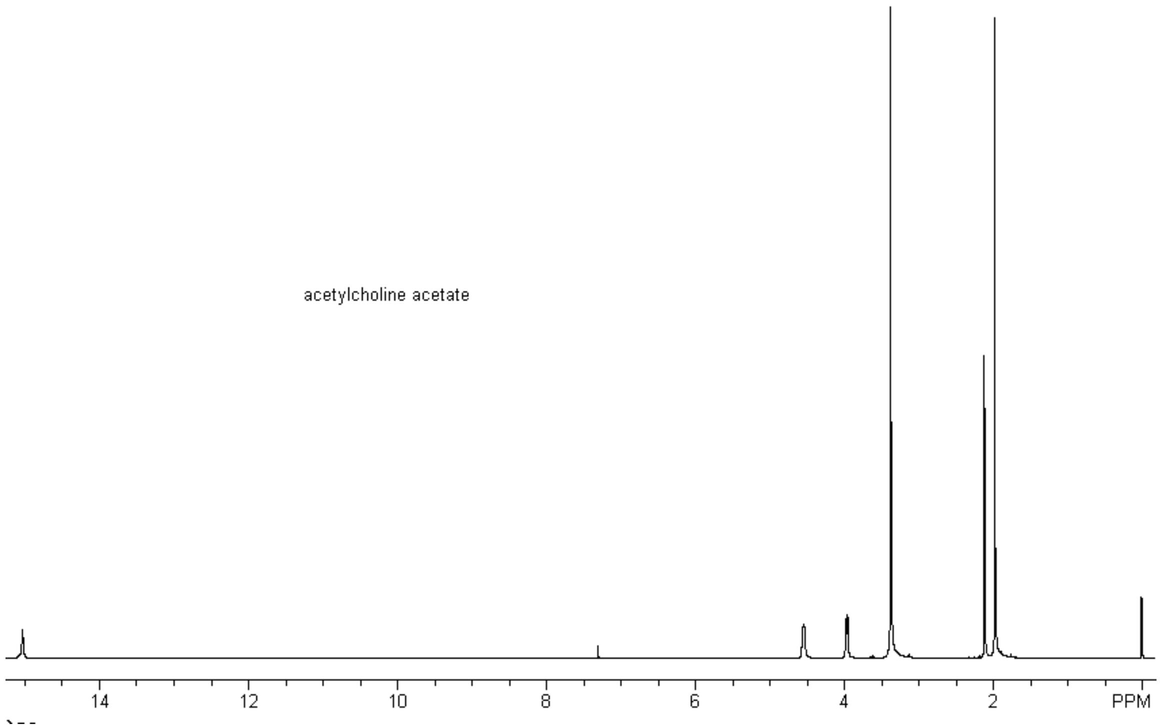
Supporting Data

Nuclear Magnetic Resonance Spectra of Selected ILs Synthesized.



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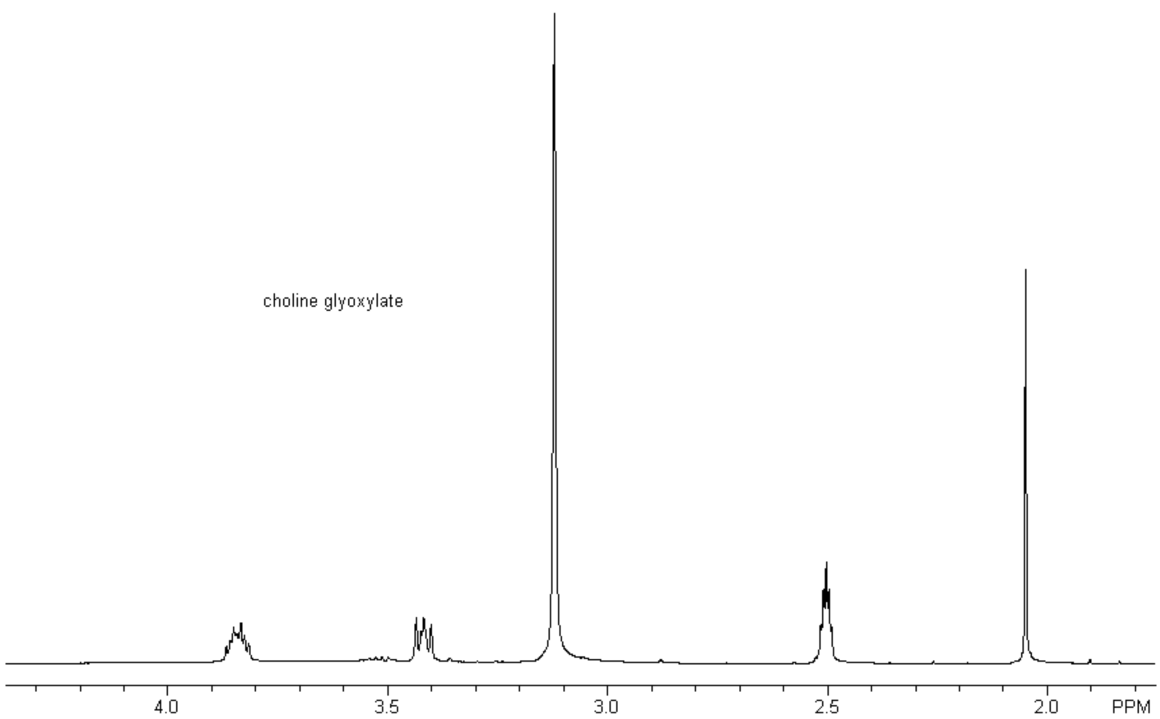
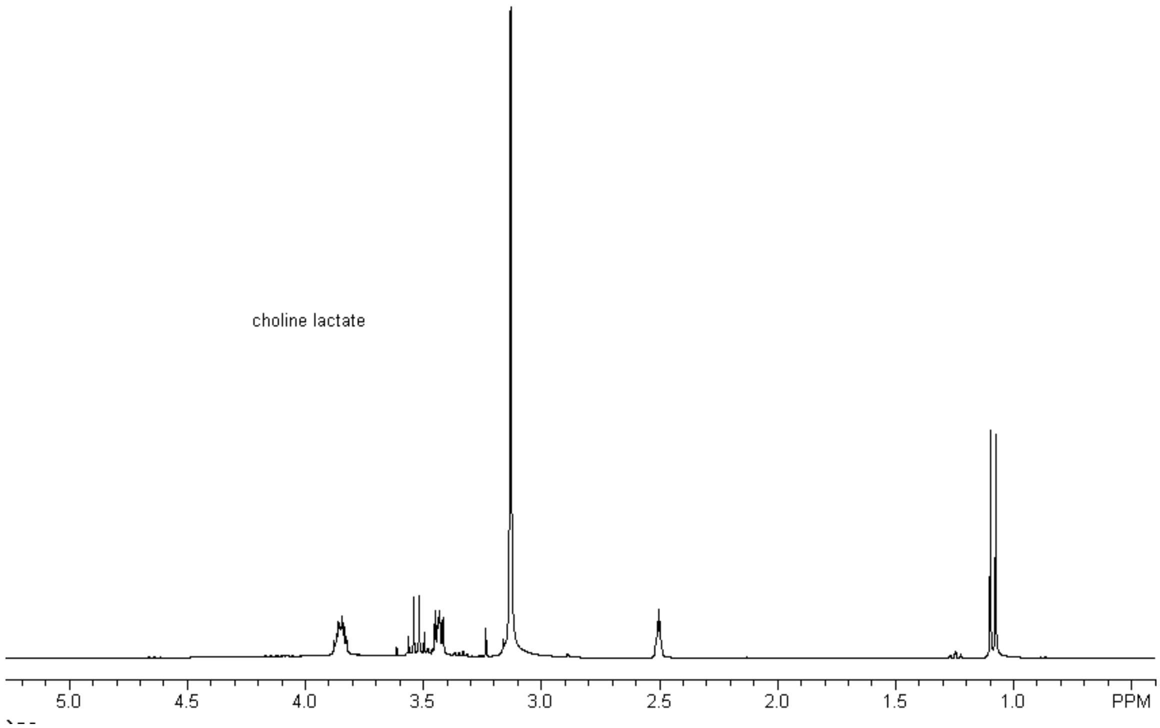
14
12
10
8
6
4
2
PPM


choline glyoxylate
4.0
3.5
3.0
2.5
2.0
PPM


choline lactate
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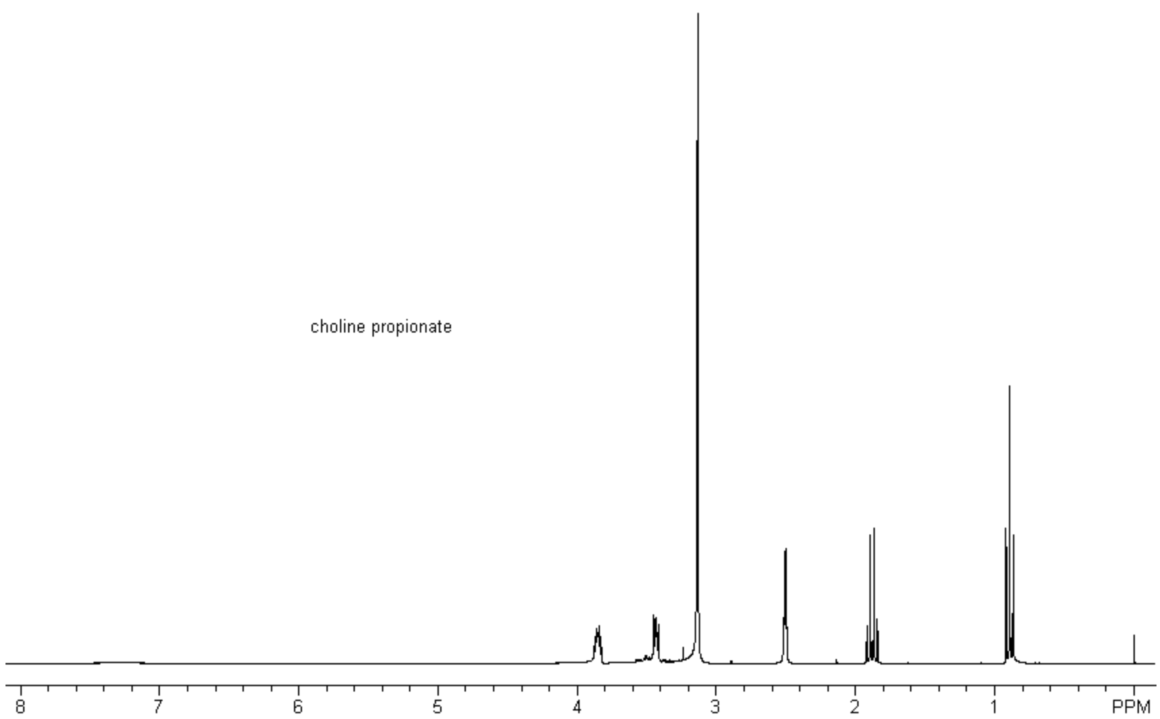
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
PPM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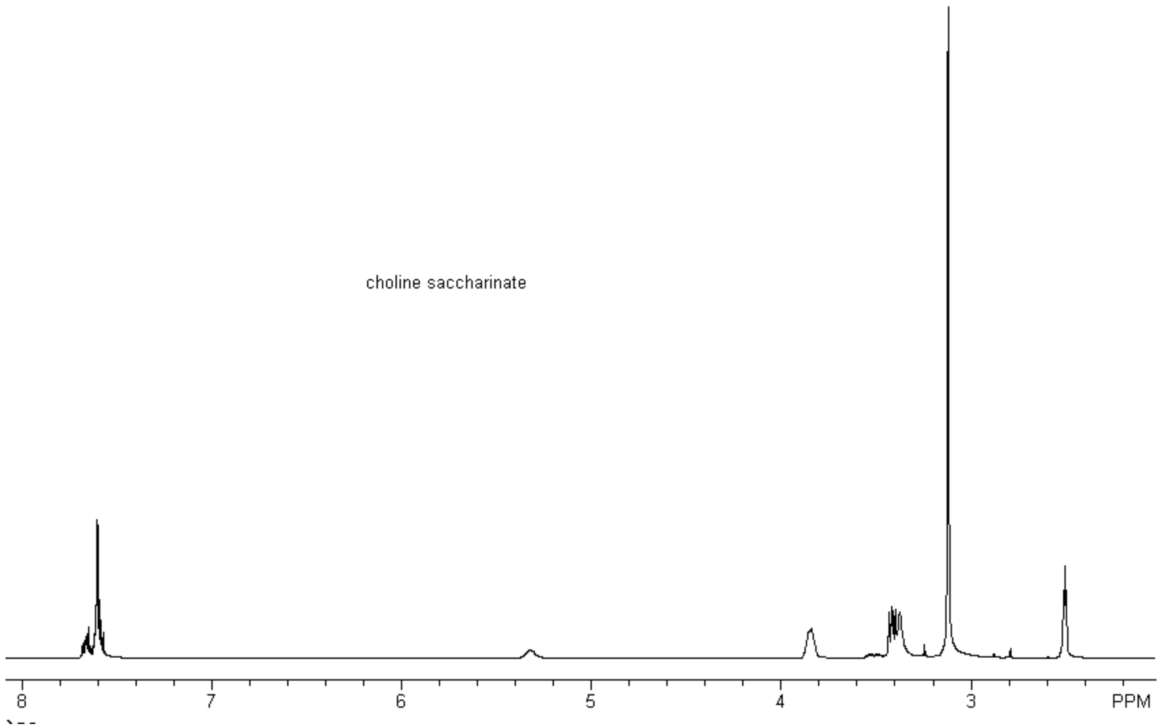
7
6
5
4
3
2
1
PPM


choline saccharinate
8
7
6
5
4
3
PPM